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CHAPTER 16

Hydrated Calcium Silicate Products Other Than Hydraulic Cements

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CONTENTS

I. Introduction

The conscious industrial utilization, by direct synthesis, of hydrated calcium silicates is nearly as recent as the understanding of their nature and properties. The industrial developments have so far, for the most part, been along empirical lines completely independent of the fundamental chemical and physical investigations. With the increasing knowledge of these compounds, and wider understanding of the manner

in which the effects of conditions of manufacture determine the particular calcium silicate produced, there is potential of wider utilization.

The hydrated calcium silicate now being formed by mankind each year amounts to some hundreds of millions of tons. Indeed, with the possible exception of the anhydrous aluminosilicates, formed in clay bricks and other ceramic products, the amount of tobermorite and related phases made exceeds that of any other chemical compound. The greater part of this large annual production is formed in concrete and mortars in the setting and hardening of Portland and other hydraulic cements dealt with in other chapters. Apart from this, however, very considerable amounts are made by direct synthesis in the following ways.

(a) Production of calcium silicate bonded building units, including sand-lime bricks, flint-lime bricks, lime-based aerated concretes, building boards and the like, all hardened by hydrothermal synthesis of the silicate from lime and silica.

(b) Production of calcium silicate bonded thermal insulating materials, using hydrothermal synthesis.

(c) Production, generally by precipitation, of finely divided calcium silicate fillers.

(d) Formation as a product of the lime–clay reaction, in the use of lime for soil stabilization in road construction.

These processes, the technical properties and qualities of the products formed and the relation of these properties to the chemistry and constitution of the hydrated calcium silicates themselves, so far as is at present known, will be considered in this chapter.

II. Calcium Silicate Bonded (Sand-lime) Bricks

Bricks composed of sand and lime, hardened by curing in high-pressure steam, with formation of a hydrated calcium silicate bond, were first made commercially in Germany about 1898, although patents covering such a process were taken out by Van Derburgh in England in 1866 [1] and by Michaelis in Germany in 1880 [2]. The English term "sand-lime brick", applied to these products before the nature of the hardening process was known, is somewhat misleading and is now being slowly replaced in the industry by the term "calcium silicate brick". This term has the advantage of including a wider range of products of the same class now being made, where siliceous materials other than sand are used. The German term "Kalksandstein" and the French "briques silicocalcaire" are both clearly descriptive.

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widely from one country to another, depending upon a number of factors. The relative availability of suitable sand, of suitable clay for clay brick-making and of gravel or stone or by-products from industry for use as concrete aggregate, has been the dominant factor. Tradition in building has also been significant in its effects; areas where the tradition has been stone block construction have more readily adopted concrete block than brick; areas where timber has been traditional have more readily adopted the aerated concretes, to obtain the equivalent insulation.

TABLE I

The annual production of calcium silicate (sand-lime) bricks (millions)

Year	United Kingdom	Germany	Holland	U.S.A.	U.S.S.R.
1900	—	300	—	—	—
1910	—	1600	120	—	—
1927	—	—	—	320	—
1930	100	1600	—	191	—
1933	—	—	600	—	—
1934	—	—	—	11	—
1935	108	—	—	—	—
1940	200	2600	—	—	—
1950	123	1000[1]	—	—	—
1956	132	—	—	—	—
1960	223	3290[1]	1000	[2]	6000

[1] W. Germany only.
[2] No figures available, but believed to be less than 50.

Table I shows the production in some countries for which figures are available. In parts of Germany, where suitable sand is widely available and other raw materials are not, calcium silicate bricks have achieved a dominant position among structural building materials, both for internal and external work. In Holland, also, the production is very large; there, however, clays from which attractive and good quality facing bricks can be made are also available and the calcium silicate bricks are used almost entirely for backing or internal work, with clay facings externally. In Great Britain common clay bricks can be produced at relatively low cost because of the availability of carbonaceous clays and shales containing part of the fuel necessary for burning the bricks. The calcium silicate brick industry has therefore not grown rapidly in size but has been forced to concentrate upon the better quality products

for facing work and other special uses. It has therefore probably given greater attention to research into the factors affecting quality than the industry has in most other countries.

In parts of the U.S.S.R. the position has been similar to that in Germany, with wide availability of suitable sands, and this class of brick is now used in great quantities; few figures of production are available, however. In the United States of America, on the other hand, the sand-lime brick is now little used. Production reached a peak in the 1920–30 period at about 320 million bricks a year but has since receded to a very low current figure with the continued growth in use of concrete block; clay brick production has receded similarly. In other countries production is at present relatively small but there is a growing potential in some of the less well developed countries.

The description given in the following pages of the properties of calcium silicate bricks and the important factors in their manufacture, is necessarily brief. More detail on some of these matters and information regarding the use of this class of brick has been given elsewhere by the present author [3].

The more important properties of building bricks or blocks are listed in Table II, with an indication of the commercial range for calcium silicate bricks, compared with the ranges for clay bricks, and for lightweight concrete and dense concrete bricks or blocks. It is apparent from this table that in general the calcium silicate bonded material compares favourably with the competitive products, although inevitably each material has its relative advantages and disadvantages.

It is clear from this table that, when properly utilized, the strength of the calcium silicate bond formed by hydrothermal reaction of lime and silica can be as effective as that derived from the hydration of Portland cement or from high-temperature ceramic bonding. The influence of the various factors in manufacture upon the effectiveness of bond and thus upon strength development is considered later. The knowledge of such factors makes it possible to produce material of any required strength within the range given in Table II. Manufacturers having such knowledge, therefore, frequently make a number of closely controlled grades of brick of specified compressive strength, in steps of 1000 lb/in², e.g. 2000, 3000, 4000 and 5000 lb/in²;† from these the grade most suitable for a given job can be chosen. The close control of strength enables the architect to design buildings with minimum wall thicknesses without fear that some of the bricks used may be appreciably below the strength on which he has based his design.

Most materials shrink slightly when dried and expand when wetted.

† Strengths in this chapter are given in lb/in²; 1 lb/in² = 0·070307 kg/cm².

The drying shrinkage is one cause of cracking in buildings, since materials are usually wet when the building is erected and ultimately dry out during prolonged warm dry weather and as a result of heating of the building. The drying shrinkage of building materials varies very widely, being zero in metals and glass and a maximum with organic materials.

TABLE II

The normal range of properties of building bricks and blocks

Property	Calcium silicate bricks	Clay bricks	Concrete bricks (dense)	Aerated concrete block (auto-claved)	Light-weight aggregate concrete block
Strength Compressive strength (lb/in²) tested in a wet condition	1500– 8000	1500– 12000	1000– 5000	300– 800	300– 2500
Volume stability Drying shrinkage (per cent of length)	0·01– 0·035	0·00– 0·015*	0·02– 0·05	0·05– 0·10	0·04– 0·08
Thermal conductivity (k) (B.t.u. ft^{-2} hr^{-1} in^{-1} deg F^{-1})	8– 11	5– 9	7– 12	0·7– 1·5	1·0– 5·0
Durability under severe natural exposure	Good if strength above 2000 lb/in²	Excellent to very poor†	Good to poor†	Good	Good to poor†
Fire resistance	Good	Very good to moderate†	Good to poor†	Very good	Very good to poor†
Properties affecting laying and plastering	Good	Varied; good to poor†	Good	Good	Good
Liability to efflorescence (soluble salts)	None	Vary from none to severe;† fairly common	None or slight†	None or slight†	Generally none
Density (lb/ft³)	105– 130	90– 150	110– 140	25– 55‡	40– 100

* Clay bricks have sometimes a small but significant progressive expansion, more particularly during their early life.

† According to quality and type.

‡ Aerated concretes are normally made to a closely controlled density at a specified value within this range. The most widely made grades have densities of 45–50 lb/in².

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Timber shrinkage may be as high as 7% across the grain, although only up to 0·2% along the grain. The figures for the various materials shown in Table II seem small compared with this; they are nonetheless significant in brittle structures where there is little elastic movement. Calcium silicate bricks have drying shrinkages below the values obtained with concrete products but generally higher than those normally found with burnt clay products. It is therefore important in manufacture to keep the drying shrinkage as low as possible, and in use to design the building and utilize techniques of construction so that stresses arising from any shrinkage are minimized.

Thermal conductivity of a building material [4] is of primary importance as affecting heat losses and thus heating costs. Generally, it is a function of the bulk density of the unit and the chemical nature of the constituents have relatively little influence upon the value. A material which is essentially of crystalline structure tends to have a slightly higher conductivity than one that is partly glassy, so that sand-lime bricks have slightly higher conductivity than clay bricks of the same density; the difference is not, however, sufficient to be of any practical significance.

While it is obvious that building materials must have good durability, it is not at all easy to define either the requirement or the ability to fulfil it. The requirements depend [5] upon the way in which the material is to be used and the conditions to which it will be exposed. Thus, they are very different, for example, for bricks (a) in an internal wall, (b) in an external wall with eaves protection and (c) in a parapet coping; bricks which might fail in one or two years under condition (c) might be quite satisfactory for 50 years in the protected external wall (b) and for ever in the internal wall (a). Calcium silicate bricks have only been made for about 60 years, but experience in practice and practical trials under severe conditions have shown the better qualities to be very durable even for use in positions of severe exposure. Since all bricks of this type have similar pore structure, the resistance to frost action is dependent mainly upon the effectiveness of bonding, i.e. upon the strength. Bricks with a compressive strength, tested in the wet condition, of more than 3000 lb/in² can be regarded as suitable for the more severe conditions of exposure, and those of more than 2000 lb/in² as suitable for normal external facing work.

The hydrous calcium silicates have, as shown elsewhere, a very small but real solubility in water and can be completely decomposed by dilute acids. Calcium silicate bonded bricks cannot normally, therefore, be regarded as suitable for use where exposed to flowing water, to one-sided water pressure, or to acids. This solubility effect is not sufficient to have

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The fire resistance of calcium silicate bricks is good; in practice, sand-lime brick walls of burned out buildings have often been in sufficiently good condition for incorporation in rebuilding. There is a considerable reduction in strength of those parts of the material reaching a temperature above 575° C, the α–β quartz inversion temperature, due to the expansion on inversion, but this drop in strength is not sufficient to cause collapse or disintegration. The softening temperature of the bricks is much above anything reached in a normal fire, and sand-lime bricks are, in fact, sometimes used for refractory purposes. They are suitable for, and are used for, chimneys, furnace casings, flues, etc. The calcium silicate bonding material itself is dehydrated at high temperatures, as shown in Volume 1, Chapter 5, but the dehydration products, which are most likely to be wollastonite ($CaO.SiO_2$) or rankinite ($3CaO.2SiO_2$), have themselves a bonding value.

A. THE FACTORS AFFECTING QUALITY OF CALCIUM SILICATE BONDED BRICKS

The factors influencing the strength of sand-lime bricks have been the subject of numerous papers [3, 6–9] and are, so far as the established procedure of manufacture is concerned, for the most part now clearly known. The major factors and their effects are described in the following paragraphs. Unless otherwise indicated, the strength values quoted are compressive strengths on small cylinders prepared in the laboratory and soaked in water for 24 hr before testing in the wet condition. Strengths on such cylinders are usually a little below those of full size bricks made on a commercial plant from the same mix and under the same nominal conditions, also tested wet.

1. Lime Content

The strength obtainable with any product consisting of a strong aggregate and a strong binding agent increases with content of binding agent, at first rapidly, until all the surfaces of aggregate are bonded and a minimum of voids is achieved, then slowly, with possibly a slight decrease with very high proportions of binder, depending upon the relative inherent strengths of the two materials and of the bond one to another.

This form of relation holds for the lime content in calcium silicate bonded materials, and Fig. 1 shows a typical curve for a sand–lime mix, in this instance with a rather fine and uniform sand [10]. The values of

the maximum strength point, both in respect of actual strength and optimum lime content, depend mainly upon the characteristics of the sand. Thus, a coarser sand would have both lower optimum lime content and lower maximum strength, while a sand of similar median particle size but better grading would give a similar or higher optimum lime content and higher strengths. Within the normal range of lime content (4–12% CaO) the strength is generally so related to lime content that it can be taken for practical purposes as directly proportional.
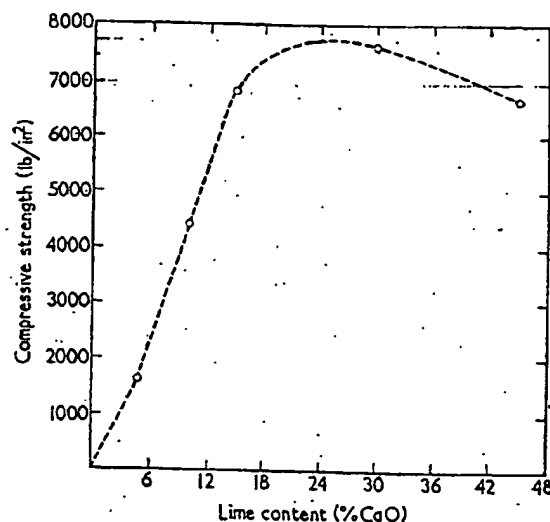

Fig. 1. An example, for a given fine sand, of the effect of lime content upon strength of sand-lime brick.

2. Lime Quality

It is generally desirable for the lime used to be a high-calcium lime of reasonable purity [11, 12]. Expansion of any hard-burnt MgO in limes of high MgO content is likely to give trouble on hydration in the auto-clave. Generally, 3% MgO is taken as a limit, but Wuhrer, Steyer and Rodermacher [13] have recently shown that, if the lime is lightly burnt, considerably higher amounts can be tolerated. The other significant impurities in lime produced from natural materials (limestone or chalk) are silica, alumina and iron oxide, mainly present as their calcium compounds. These impurities are only of indirect importance in that they reduce the amount of calcium available to form the calcium silicate bond.

The alumina present as gehlenite ($2CaO.Al_2O_3.SiO_2$) is inert, but any present as calcium aluminate may form hydrogarnet ($3CaO.Al_2O_3.(SiO_2, 2H_2O)_3$), which takes up a relatively high proportion of lime and has no bonding value.

Any unburnt limestone or chalk in the lime acts as a diluent or filler and is significant only as reducing the amount of useful or "available" lime. The latter is determined by a recognized empirical titration method, which in effect gives the amount of calcium which is present as free calcium oxide or hydroxide or which is readily formed by hydrolysis of calcium silicates etc. The available lime content thus serves as a useful control test of the value of a lime for this purpose.

3. Sand or Aggregate Quality

The nature and quality of the sand or other aggregate used is, in practice, the most important factor affecting quality. The grading of
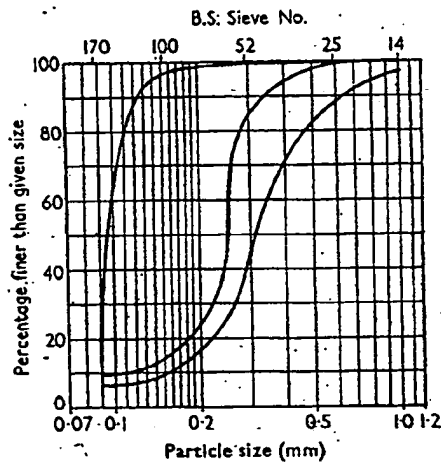

FIG. 2. The grading of typical natural sands used in calcium silicate bonded (sand-lime) bricks.

particle size, the particle shape, the surface characteristics and the quantity and nature of any mineral matter other than quartz, or of other impurities, may each have very great effects upon the properties of the brick.

A wide range of particle size is desirable for good results, the maximum size of grain and the amount of coarser material desirable depending

upon the texture required and upon limitations induced by problems of pressing the units; generally, a maximum size of about $\frac{1}{4}$ in (6 mm) can be tolerated. At the other end of the size scale, presence of an appreciable proportion of fine silica flour is advantageous; indeed, very high strengths can be achieved only when there is a fairly high content of very fine silica. The grading curve should be such as to give a low porosity when compacted; this may be achieved either with continuous grading or gap-grading. Most natural sands are closely graded and do not therefore satisfy these conditions. It is therefore often advantageous to blend
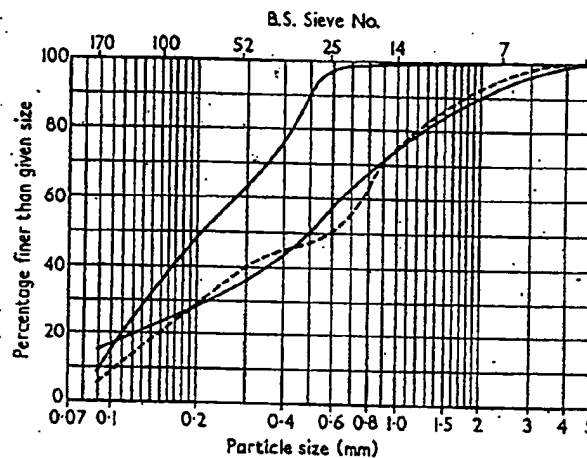

FIG. 3. The grading of samples of blended sands, or of crushed flint and sand, used to give high-strength calcium silicate bonded bricks.

two different sands or other fine aggregates of different average particle size or to grind a portion of the sand, if it is originally coarse enough, in order to broaden the range of sizes. Figure 2 shows the grading curves of some natural sands used in calcium silicate brick manufacture. Figure 3 shows some grading curves of blended sands or crushed flint and sand used to give higher strength bricks. Although detailed consideration of the procedures is outside the scope of this book, the grading, where the available raw materials permit, can now be designed to enable the producer to make bricks of any required strength within the normal range of needs.

The sand used also affects the drying shrinkage of the bricks, the three factors involved being the amount of clay impurity, the fineness and the surface characteristics of the sand grains.

4. Pressing Conditions

The materials for calcium silicate bricks are mixed to a damp condition, the amount of water being such that the mix just coheres when squeezed in the hand. The water content varies somewhat with the fineness of the aggregate and with the lime content, but is generally between 4 and 7%. It is not highly critical up to an optimum value, but if this amount is
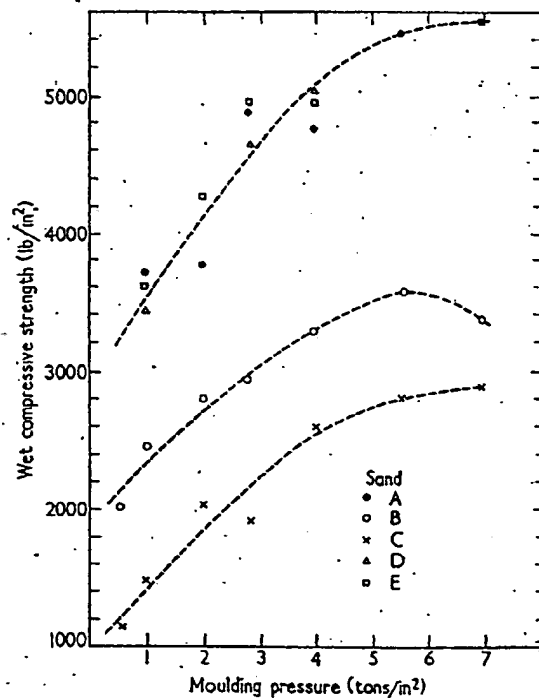

FIG. 4. The effect of moulding pressure upon the strength of sand-lime bricks.

significantly exceeded, bursting of the bricks and even complete collapse of the whole mass of bricks can occur in the autoclave.

The moulding pressure normally used is about 2–3 tons/in^2, i.e. about 100 tons on each brick. The machines have therefore to be very robust and the wear on the liners of the brick moulds is very severe. These high moulding pressures are necessary to achieve, with these non-plastic mixes, the degree of compaction necessary. Figure 4 shows the variation
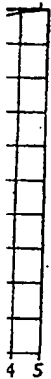
of strength with moulding pressure for several sands. From these results it would appear to be worth while increasing pressures to about 4 tons/in². In practice, however, the additional cost of the machine and the increased maintenance costs make this a less economic method of achieving increased strength than other methods.

5. The Conditions of Steam Hardening (Autoclaving)

The conditions of steam hardening used in commercial practice are determined primarily by economic considerations. These include the
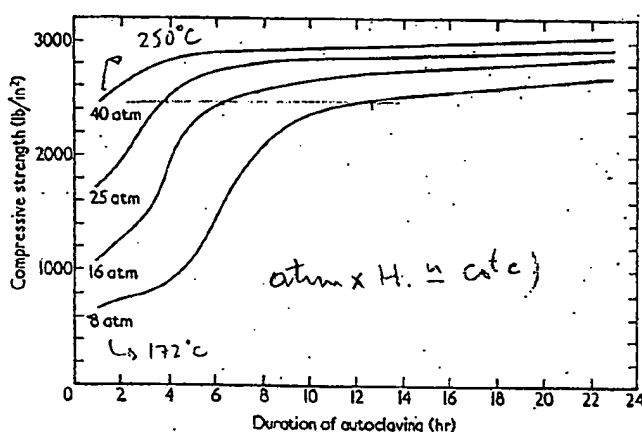

FIG. 5. The effect of duration of steam hardening (autoclaving) upon the strength of a calcium silicate bonded brick (6% CaO content) at various pressures, after Gunzelmann [8].

amount of fuel required, the capital cost of the plant needed and its throughput, and the labour involved. The extremes of conditions used range from about 20 hr at full steam pressure, with the lowest pressures of about 8 atm (120 lb/in²), down to about 2 hr at pressure with the highest pressures of about 25 atm (350 lb/in²). The very high pressures have been used only in a very few recent plants in Germany, the normal range both in the U.K. and abroad being from 8 to 13·5 atm (120–200 lb/in²). It has been shown by several investigators [8, 14, 15] that over the practical range of steam pressures the same degree of hardening, as measured by the compressive strength of the product, can be obtained by varying the time appropriately. The curves in Figs. 5 and 6 illustrate this. It is also apparent from Fig. 5 that for each pressure there is a

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steaming time beyond which the gain in strength is no longer sufficient to justify the additional cost of further steaming. It is usual therefore to find that a plant operates on a fixed time of steaming, depending upon the designed working pressures of the boiler and of the autoclaves.

Going beyond the periods of autoclaving used in commercial practice, Pohl [15] has shown, in tests at 8, 16 and 21 atm autoclave pressure, that at the higher hardening pressures, although the increase in strength takes place at a higher rate, the maximum strength achieved is lower; if hardening is continued too long, a reduction in strength is liable to occur.
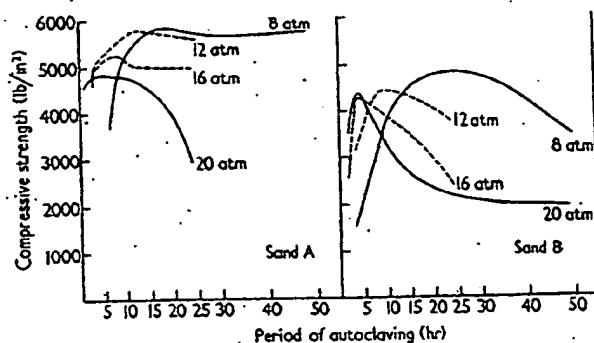
FIG. 6. The effects of time and pressure of autoclaving upon strength of sand-lime bricks (periods up to 48 hr).

These conclusions, which did not appear from Gunzelmann's work, have been confirmed by the present author, and the curves of Fig. 6 show the values obtained with two different sands, with 10% hydrated lime. It will be noted that the drop in strength with long periods of autoclaving is much more marked with one sand than with the other. The causes of these lower strengths at higher pressures have not yet been proven, but they are no doubt due to changes in the hydrated calcium silicate, which may be either a change in the crystal form or structure of the tobermorite or an inversion (for example, to xonotlite), as discussed in the next section of this chapter.

B. The Constitution and Microstructure of Calcium Silicate Bricks

Despite the very large amount of fundamental work on the hydrated calcium silicates themselves, there has been relatively little on the microstructure and constitution of the actual bond in calcium silicate bricks. Early investigators [16, 17] in optical microscope studies observed

both crystalline and amorphous material, but it is not now clear how much of the crystalline material observed was calcite.

Smirnov [18] in 1926 reviewed earlier work and showed the presence of a hydrated silicate as fine "scales" of low birefringence with refractive indices between those of quartz ($\omega = 1\cdot544$) and microcline felspar ($n_m = 1\cdot523$). He observed also that the silicate was readily converted to carbonate (calcite) on exposure, so that in old bricks much, if not all, of the lime content was present as carbonate. His analyses, for lime, soluble silica and carbonate content, show, after allowing for $CaCO_3$, the molar ratios in the silicate given in Table III.

TABLE III

The range of composition of the bonding material in sandlime bricks

Author	Ratio of combined lime to soluble silica	Ratio of combined water to soluble silica
Smirnov [18]	0·99–1·27	1·65–1·99
Bessey [3]	0·97–1·77	—
Bessey [55]	0·83–1·86	0·88*–2·22*
Kalousek [22]	0·99–1·75	—

* Dried *in vacuo* at about 80° C.

Grime and Bessey [19] in 1933, from X-ray, chemical and optical examination, concluded that the bonding agent was an amorphous hydrated calcium silicate, but the equipment and the information available to them were inadequate to show the more diffuse patterns of tobermorites or to distinguish them in the presence of calcite and quartz. The Building Research Station published in 1939 [20] photomicrographs showing that in some commercial bricks the bonding material was amorphous, so far as resolution in the optical microscope could show, but that in others (rather uncommonly) there was a fine short needle-like growth of crystals. Plate 1 shows one of these photomicrographs of the crystalline material. Unfortunately, no X-ray diffraction results were obtained on this material.

Bessey [3] in 1948 indicated that the more crystalline silicate bond was found in bricks made with sand which, because of some undetermined grain surface condition, was less reactive than that which gave the more amorphous bond. The bricks containing the more crystalline material had lower drying shrinkage. He found in this work, done in 1938–9, that the lime/combined silica ratios in a range of 21 different commercial

TABLE IV

The amount and composition of the bonding material in some commercial calcium silicate bricks [55]

Determined values		Calculated values	
		Molar ratio of combined	Calculated compressive strength
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TABLE IV

The amount and composition of the bonding material in some commercial calcium silicate bricks [55]

Sample No.	Total lime (as CaO) (%)	Combined silica (as SiO₂) (%)	Free lime (as CaO) (%)	Loss at 1000°C (%)	Carbon dioxide (%)	CaO as silicate (%)	Silicate cementing material (%)	Molar ratio of combined lime to combined silica	Molar ratio of combined water to combined silica	Compressive strength of bricks (lb/in²)	Calculated compressive strength for each 1% soluble silica
18	14·08	15·67	0·07	4·86	0·71	13·11	32·92	0·80:1	0·88:1	6768	430
17	12·08	12·98	0·08	4·93	0·63	12·12	29·38	1·00:1	1·10:1	6468	420
19	12·88	12·27	0·07	4·88	0·70	11·91	28·34	1·04:1	1·13:1	4355	360
63	9·78	8·78	Nil	4·33	0·57	9·06	21·60	1·12:1	1·43:1	2380	270
16	9·01	8·66	0·01	4·36	0·41	8·68	21·29	1·07:1	1·52:1	3135	360
131	8·70	7·90	Nil	3·87	0·10	8·57	20·24	1·16:1	1·59:1	6870	870
22	9·24	8·64	0·07	3·66	0·64	8·36	19·90	1·05:1	1·17:1	4030	470
61	8·02	7·15	Trace	3·76	0·42	7·49	17·98	1·13:1	1·54:1	3740	520
32	7·92	7·91	Trace	2·97	0·75	6·97	17·10	1·13:1	1·54:1	5210	660
20	7·59	6·10	0·01	3·58	0·49	6·96	16·10	0·94:1	0·94:1	6130	840
65	7·32	8·25	Trace	3·49	0·46	6·74	16·02	1·22:1	1·86:1	5560	880
29	7·39	6·05	0·04	3·19	0·55	6·65	15·33	1·16:1	1·62:1	5030	830
133	6·91	6·28	Nil	3·26	0·55	6·21	15·20	1·18:1	1·45:1	5550	880
132	5·76	7·25	Nil	3·07	0·64	4·95	14·68	1·06:1	1·44:1	5410	750
181	8·07	5·00	0·12	4·64	1·27	6·34	14·57	0·83:1	1·26:1	1480	300
21	5·93	6·58	Nil	2·49	0·51	5·28	13·84	1·36:1	2·22:1	4508	680
33	6·73	5·00	Trace	3·04	0·99	5·48	12·53	0·86:1	1·00:1	2520	500
34	6·99	4·03	0·01	3·75	1·47	5·12	11·43	1·18:1	1·36:1	1620	400
46	4·44	4·55	Nil	3·02	0·64	3·63	10·58	0·86:1	1·70:1	5480	1200
28	7·60	3·72	1·25	3·83	1·40	4·57	10·30	1·31:1	1·80:1	1308	350

bricks varied over the range given in Table III. The more recent results by the present author, derived from Table IV, are also given in Table III.

Taylor [21] in 1952 reported X-ray evidence of the presence of a tobermorite-type compound in a commercial lightweight sand-lime block; the lime/soluble silica ratio in this material was 1·28. Kalousek [22], using X-ray diffraction, differential thermal analysis and soluble silica determinations on lime:sand specimens made up and autoclaved under a
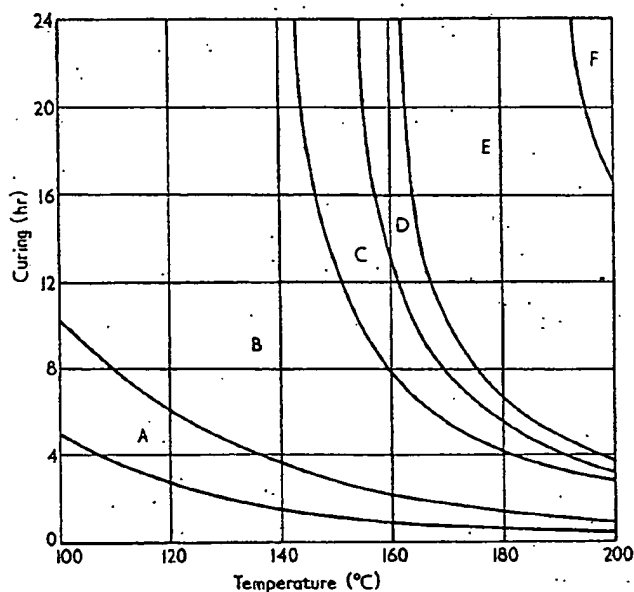

FIG. 7. The phases detected in autoclaved lime-quartz pastes (Neese [26]).
A—$C_{1·75}SH_n + Ca(OH)_2$ + quartz;   B—$C_{1·25}SH_n + Ca(OH)_2$ + quartz;
C—$C_{1·25}SH_n$ + quartz; D—$C_{1·0}SH_n$ + quartz; E—$C_{1·0}SH_n$ + tobermorite
+ quartz; F—tobermorite + quartz.

variety of conditions, found (Table III) lime/soluble silica ratios similar to those found by Bessey. When the ratio was below 1·3 only tobermorite was found, but when the ratio exceeded this figure the DTA results indicated gradual crystallization of α-dicalcium silicate hydrate. Further work [23, 24] showed that the reaction proceeded through a series of steps, starting with the formation of badly crystallized C-S-H (II) having a high lime/silica ratio, followed by C-S-H (I) with a lower lime/silica ratio and crystalline tobermorite. Neese and his co-workers [25, 26], using chemical, optical, X-ray, DTA, thermogravimetry and

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dilatometry methods on autoclaved pastes of lime and finely divided quartz, came to similar conclusions. Figure 7 shows an example of the results reported for the phases found over the range of temperatures and times commonly used in calcium silicate brick manufacture. The positions of the curves defining the various areas are not precise and must vary with the lime/silica ratio of the mix and the surface area of the silica, but they show clearly the progressive changes that occur.

Aitkin and Taylor [27] examined products of lime–quartz pastes over a CaO/SiO_2 range of from 0·33:1 to 3·00:1 at autoclaving temperatures from 90° to 200° C (1–15 atm pressure) and observed the formation of the compounds shown in Table V.

TABLE V

Compounds detected in lime–quartz pastes (Aitken and Taylor [27])

Compound	Overall CaO/SiO_2 ratios of pastes in which detected	Range of temperatures in which compound was formed (°C)
Gyrolite	0·33–0·67	165–200
C-S-H (ill-crystallized)	0·33–3·00	90–175
Tobermorite (crystalline 11 Å form)	0·33–1·08	125–200
Xonotlite	0·67–3·00	165–200
"Phase F"	1·00–3·00	155–200
α-C₂S-hydrate	1·50–3·00	125–175
Hillebrandite	1·67–2·00	165–200

Quincke [28] published some excellent electron micrographs showing the action of the lime on the quartz surface and the formation of matted fibres, probably of tobermorite. He also gives electron diffraction patterns which, he suggests, show formation of 11·4 Å tobermorite and of gyrolite.

The general picture of existing knowledge on the lime–quartz reaction as occurring in the process of hardening of calcium silicate bonded bricks, ignoring for the moment the effects of the impurities which are inevitable in industrial raw materials, has been clearly summed up by Taylor [29] as follows:

"Although many details of the lime–quartz reaction in pastes are still obscure, and others depend on the precise working conditions, the general picture seems now to be fairly clear. Reaction on the surfaces of quartz grains yields initially a lime-rich poorly crystallized tobermorite mineral, similar in composition to C-S-H (II) made in suspensions. When the

overall Ca/Si ratio is low, this reaction proceeds until all the lime is used up; the C-S-H (II) then reacts with more quartz giving C-S-H (I), the Ca/Si ratio of which eventually drops to 0·8. If the temperature and time of autoclaving are sufficient, the C-S-H (I) recrystallizes to tobermorite and eventually to xonotlite. Tobermorite has been detected in pastes cured at 125° C and above, and xonotlite at 165° C and above, but higher temperatures are needed in each case to make the reaction proceed at a technically useful rate. If the overall Ca/Si ratio is below 0·8, the C-S-H (I) or tobermorite also reacts slowly with the unused quartz to give gyrolite.

"When the overall Ca/Si ratio is above 1·0, C-S-H (II) is probably still the initial product. In this case, however, even before all the quartz is used up, the C-S-H (II) begins to recrystallize into other lime-rich phases. The most usual of these is α-C_2S hydrate. Crystallization of this phase is probably gradual, and there is evidence that its composition can depart from the ideal value, at least in the early stages of formation. Other lime-rich phases may also be formed but less reproducibly; further work is needed on this aspect of the problem."†

The second paragraph of this quotation refers to conditions that never truly hold for a commercial brick composition, but since the ratio of lime to *available silica* will depend upon the area of surface exposed and hence upon the fineness of the sand, it may well be that the effective ratio of Ca to Si during the period of reaction does exceed 1·0 even though the ratio of lime to total SiO_2 is probably less than 0·1.

The kinetics of the reaction of lime and quartz have so far been given little attention and very little information has been published. There is considerable variation in the rate of reaction, both with surface area of the silica and with reactivity of the surface of the sand grain. Table VI shows the amounts of silica reacted, after raising the autoclave to 10·7 atm (157 lb/in²) pressure in 1 hr and holding it at that pressure for only 15 min, with a mix of 10% hydrated lime and 90% various sands. Freshly crushed quartz crystal (samples 58, 59, 66 and 67) is more highly reactive than most of the natural sands; when, however, all particles below 100 mesh were removed, the amount of reaction in this period was small. There is evidence of a relation between the drying shrinkage of bricks made with these sands and the rate of formation of soluble silica, particularly with the pure quartz. With the most active sample of crushed quartz the amount of silica which had reacted (4·3%) in this short time was more than half of the amount which would react with long autoclaving.

The effects of the impurities in lime and natural sand upon the con-

† Nomenclature slightly altered to agree with that used elsewhere in this book.

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stitution have not been widely studied. Clay minerals are known to have adverse effects upon the properties of the bricks, probably because of hydrogarnet $(3CaO . Al_2O_3 . (SiO_2, 2H_2O)_3)$ formation. Kalousek [30] has also suggested that small amounts of alumina may, under appropriate conditions, enter the tobermorite lattice and modify its properties. Since, in the manufacture of calcium silicate bonded products generally, producers have to deal with impure natural products, further research into the effects of small amounts of the common natural impurities, i.e. clay minerals, hydrated alumina, hydrated iron oxide, magnesia, and alkali carbonates and sulphates, could be fruitful.

TABLE VI

Rates of reaction of sands with lime (proportion of silica reacted after 15 min at 157 lb/in^2 steam pressure)

	Sand sample no.	Reacted silica (SiO$_2$ %)	Drying shrinkage of bricks made with same sand with 6 hr autoclaving (%)
Crushed quartz	59	1·3	0·028
	58	2·8	0·045
	67	4·3	0·054
	67 sieved on 100 mesh B.S. sieve	0·4	n.d.
Natural sand	51	0·5	0·018
	54	1·4	0·015
	50	0·9	0·031
	64	2·3	0·028
	65	1·3	0·005
	55	3·4	0·053

C. THE RELATION BETWEEN COMPOSITION OF THE BONDING MATERIAL AND THE TECHNICAL PROPERTIES OF THE PRODUCT

While the evidence suggests that the lime/silica and combined water/silica ratios vary only over a narrow range in the bonding material in sand-lime bricks, the phase composition may vary much more than the overall chemical composition. Even within the range of tobermorite-like phases, the crystal form, the crystal size, and even the composition and cell dimensions, may all vary to such an extent that the technical properties are materially affected. In some products, xonotlite, gyrolite,

α-C_2S hydrate and perhaps other phases may replace the tobermorite-like phases and have major effects upon properties. Also, in these commercial materials the introduction into the gel or crystal structure of aluminium or other ions by isomorphous substitution may change the properties. Although much remains to be learnt of these effects, something is known of them, in particular from the work of Kalousek [23, 30] and that of Sanders and Smothers [31], as indicated below.

1. Strength

The strength of bond given by the various hydrated calcium silicates varies very widely. This variation is discussed generally in Volume 1, Chapter 11, and only the information available on those compounds which may be important in products made directly from lime and silica need be considered here.

The evidence from the observations of Menzel [32], Sanders and Smothers [31] and Kalousek and Adams [33] on the strength of Portland cement and fine silica mixes have demonstrated the relatively low strength of α-C_2S hydrate.

Kalousek and Prebus [24] showed that crystallized tobermorite gives higher strength than C-S-H (I). There is also evidence from the present author's work that a lower lime/silica ratio in the C-S-H corresponds to higher strengths, but it is difficult to separate this effect from that of the crystallization of the tobermorite.

Kalousek [34] has found satisfactory strengths with a xonotlite bond, but no direct comparisons with tobermorite are available.

2. Drying Shrinkage

The most important difference in drying shrinkage is that between C-S-H (I) and crystalline tobermorite [24]. This accounts for the substantial difference between concretes cured at ambient temperatures or in low-pressure steam and those cured in the autoclave, and for the relatively low drying shrinkage of calcium silicate bricks. α-Dicalcium silicate hydrate and xonotlite are both known to have still lower drying shrinkage than tobermorites, but there is still a wide area of uncertainty needing further study of the effect upon this property of variations within the tobermorite range of composition and with varying degree of crystal growth.

3. Other Properties

No other important technical properties of calcium silicate bricks are known to be significantly affected by the nature of the silicate bond.

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## III.   Aerated (Foamed) Calcium Silicate Products

The achievement of light weight with adequate strength and durability in structural building materials has important advantages. Commercial attempts by purposeful incorporation of gas into cement bound products before hardening, to form the class of materials which have been variously known as aerated, foamed or cellular concretes, date from about 1925.

Various methods have been used for effecting aeration, but they all fall into one of two types: (a) the generation of a gas within the mix by chemical action and (b) the incorporation of air in the mix by injection of a stable foam or by whipping in air by suitable mixing devices using air-entraining agents in the mix.

Of the chemical methods of gas generation, the reaction between fine aluminium powder and lime, to generate hydrogen gas, is most used. The lime may be present as such in the mix or may be formed in the hydration of Portland cement used as binder. Calcium aluminates are formed as secondary products, but the amounts involved are not sufficient to be significant in the setting process. Assuming formation of tricalcium aluminate hexahydrate, the following equation expresses the reaction:

$$2Al + 3Ca(OH)_2 + 6H_2O \longrightarrow 3CaO.Al_2O_3.6H_2O + 3H_2$$
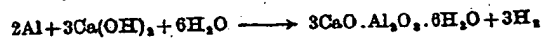
An alternative method, which has been utilized commercially, involves generation of oxygen gas by the reaction between hydrogen peroxide and bleaching powder, a mixture of $Ca(OCl)_2$ and $CaCl_2.Ca(OH)_2.H_2O$, thus:

$$Ca(OCl)_2 + 2H_2O_2 \longrightarrow CaCl_2 + 2O_2 + 2H_2O$$
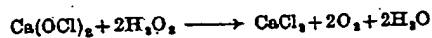
The foam injection process utilizes chemically stabilized foams similar to those used in fire fighting. By use of suitable foam generators, with which the bubble size and the amount of air to a given volume of liquid are closely controlled, and injection of a known volume of foam into a mix, any required density of product can be achieved, with good quality control. The method is, however, utilized more for aerated concretes made on the building site than for the factory-made autoclaved products.

The method in which air is whipped directly into a mix containing air-entraining agents cannot incorporate as much gas and cannot therefore achieve such low densities as the other methods mentioned. It has been used for concrete of a density down to about 80 lb/ft³.

The earliest of the aerated concretes, e.g. in the United Kingdom the material Aerocrete, were made with Portland cement, sand and aluminium powder. They were allowed to harden at ordinary temperatures and, although of reasonable strength, suffered from excessively high drying shrinkage. Later types (e.g. the Swedish products Siporex and

Ytong and the Danish Durox) were autoclave cured, the drying shrinkage being very much reduced thereby. With autoclaving it became possible to use lime instead of, or in part replacement of, Portland cement, the end-products of either bonding material being essentially the same. The choice of one or other depends largely upon economic factors and upon convenience in the process. Also, materials other than sand can be used, provided that they are sufficiently siliceous for reaction with the lime and sufficiently strong and stable in themselves. Thus, ground burnt shale (Ytong, Sweden) and pulverized fuel ash (Thermalite-Ytong and Celcon, United Kingdom) are both satisfactorily used. In order to produce material of the densities normally required, it is necessary for the aggregate to be very fine, with the greater part finer than 100 mesh (152 μ). If natural sand is used as aggregate, it is generally necessary to grind it to the required fineness.

The greater part of autoclaved aerated concrete production has in the past been in the form of building block, which, because of the lightness in weight, can be very much larger in size than the building brick, thus effecting economies in handling and in construction. The common size in most countries is equivalent to 12 bricks. More recently, however, use of large reinforced panels for wall and roof construction and in beams, lintels, etc. has become widespread. Development in this direction was at first slowed down by the need to overcome problems of corrosion of the reinforcement, which are naturally more serious than with dense concretes, but satisfactory durability is now generally accepted.

A. PROPERTIES

The aerated concretes have most often to compete commercially with lightweight concretes made by use of lightweight aggregates (clinker, foamed slag, expanded clay, sintered pulverized fuel ash, perlite, exfoliated vermiculite, etc.). A comprehensive study of both aerated and lightweight aggregate concretes including their properties and uses has been made by Short and Kinniburgh [35].

The normal range of technical properties of the aerated concretes is shown in Table II. In general, all properties are related to the density, which may be anything from about 25 lb/ft³ (400 kg/m³) upwards. In practice, grades of 30–35 lb/ft³ and of 45–50 lb/ft³ (480–560 kg/m³ and 720–800 kg/m³, respectively) are most commonly made; the former for use where thermal insulation is most important, and the latter where rather greater strength is required.

The strengths attainable are more dependent upon density than any other single factor, and, as indicated above, the densities at which these

materials are made are
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materials are made are usually fixed as low as possible consistent with the strength required. For load bearing building blocks the minimum strength requirement in the U.K. is generally taken as 400 lb/in^2 (28 kg/cm^2). Table VII shows the manner in which the strength of typical autoclaved aerated concretes varies with density; from these figures it may be seen that for the above minimum strength of 400 lb/in^2 a concrete density of at least 35 lb/ft^3 is necessary. Lower densities, with lower strengths, can be used for purposes in which the material is not load bearing.

TABLE VII

The relation between density and other properties of aerated concrete
(Short and Kinniburgh [35])

Dry density (lb/ft³)	Cube crushing strength (tested wet) (lb/in²)	Modulus of elasticity (lb/in² × 10⁶)	Thermal conductivity (k) (B.t.u. ft⁻¹ hr⁻¹ in⁻¹ deg F⁻¹)
20	—	—	0·58
30	300	0·21	0·75
40	500	0·33	1·00
50	700	0·45	1·40

The low thermal conductivity is an important property of aerated concretes, giving them an advantage for many uses over most of the alternative materials. It is almost entirely a function of density and is independent of the nature of the bonding material (cement or lime), but it is very slightly greater with sand as aggregate than with aggregates which have themselves lower inherent conductivity (p.f. ash and burnt shale). Some typical values for various densities are shown in Table VII.

The drying shrinkage of the autoclave-cured aerated concretes tends to be higher than most other material used in brick or block construction, and manufacturers have to give considerable attention to the factors involved to keep the shrinkage as low as possible. Some of the factors found empirically to affect shrinkage for material of given density are: (a) the proportion of bonding agent, which should be as low as is practicable; (b) the particle size distribution of the aggregate; (c) the autoclave curing conditions (duration and pressure) which must be adjusted by trial according to the raw materials involved to give the best values for drying shrinkage consistent with economical production.

B. Structure and Constitution

1. Structure

The macrostructure of a good aerated concrete (Plate 2) is in fact that of a solid foam with fine and nearly uniform round bubbles of air, held in a matrix of the very fine aggregate bonded together with the cementing medium. The air bubbles are in most processes originally hydrogen bubbles, but the hydrogen is rapidly lost by diffusion. The bubbles are not interconnected, except by very fine capilliaries in the matrix, and water will not penetrate to them rapidly; dry aerated concrete will float for long periods in water before sufficient water penetrates to allow it to sink. This difficulty of saturation with water and the peculiar distribution of pore sizes together account for the remarkably high resistance to frost action of aerated concretes compared with other materials of similar strength. Even distribution of bubbles and uniformity of size are objectives which the manufacturer seeks to achieve, since the formation of some larger bubbles or the presence of irregular layers leads to lack of uniformity of quality of the product and to unsatisfactory mechanical and physical properties. It is also sought to ensure sphericity of bubbles since elliptical bubbles tend to cause variation of strength in different directions. The measures taken to control and ensure this uniformity and isotropy of structure are part of the closely guarded know-how of firms which have developed these materials.

The microstructure of the matrix of material, in which the air voids are embedded, is essentially the same when lime is used as the binder as in the dense calcium silicate bonded bricks, except that the aggregate is much finer. There are no published observations of crystalline structure visible in the optical microscope, and, because of the much higher surface area of the aggregate and the correspondingly higher rate of reaction of the lime and silica, it may be that the conditions for such visibly crystalline growth do not occur.

2. Phase Composition

Very little has been published on the phase composition of the bonding material in the aerated concretes, whether made with lime or Portland cement as binder. The examination by Taylor [21] of an aerated sand-lime block, in which he found a crystalline tobermorite and a $CaO.SiO_2$ ratio of 1·28, has already been mentioned. In general, however, essentially the same course of phase formation may be expected as for the dense calcium silicate bonded bricks when lime is used with ground quartz sand as aggregate, and essentially the same as with autoclaved dense Portland cement concrete products when this cement is used.
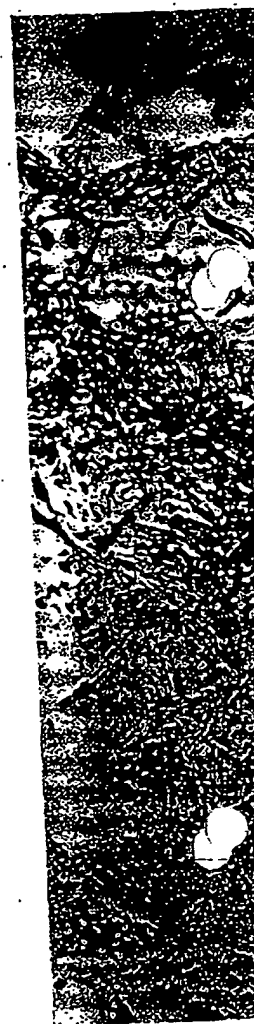

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PLATE 1. Photomicrograph of calcium silicate bonded brick, showing needle crystals of hydrated calcium silicate (× 1620, ordinary light).

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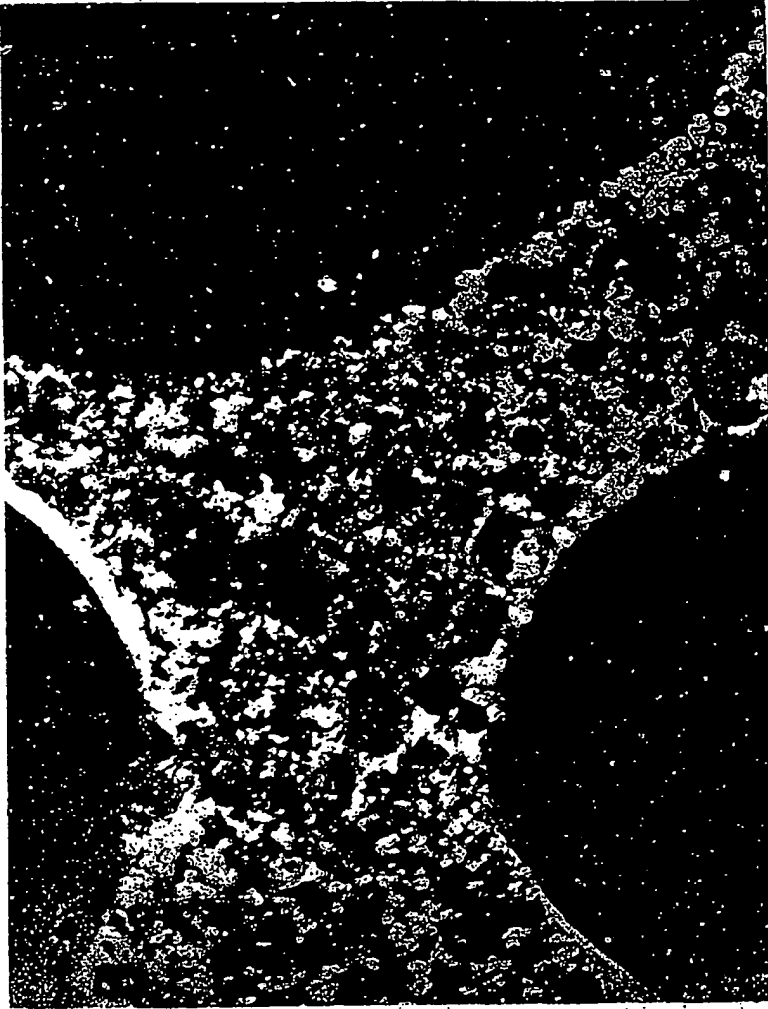board are given in Table
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PLATE 2. Photomicrograph of aerated concrete, showing solid foam
structure. (× 410, crossed nicols)

IV. Calcium Silicate Bonded Asbestos Products

Direct synthesis of hydrated calcium silicate from lime and silica is used in the manufacture of a variety of proprietary materials with asbestos as the aggregate or as reinforcement. These range from dense, hard, and strong sheet materials used for wall and ceiling linings, particularly in ships (where their high fire resistance is valuable), to extremely lightweight materials in slab or moulded form, used for the thermal insulation of pipes, boilers, etc. The processes used for the manufacture of these materials are proprietary, and little has been published regarding them, except in trade literature.

TABLE VIII

Properties of calcium silicate bonded asbestos products [1]

Type	Density (lb/ft³)	Thermal conductivity at given temperature		Maximum temperature of use	
		(°F)	(B.t.u. ft⁻¹ hr⁻¹ in⁻¹ deg F⁻¹)	(°F)	(C°)
A. Lightweight calcium silicate insulation	11½	200	0·36	1200	650
		400	0·46		
		600	0·56		
		800	0·65		
B. Calcium silicate bonded insulation board	44–48	Ambient	0·75	1000	540

[1] From data quoted by manufacturers.

Diatomaceous earth, a highly reactive form of silica, is used with lime, asbestos and other ingredients in making most of these materials. In some types use is made of the fact that a sufficiently rapid reaction takes place between lime and diatomaceous earth, at temperatures approaching 100° C, to cause within a few minutes a gelling of a mixture of these ingredients when poured into steam-heated moulds. The stiffening is sufficient to allow the moulded products to be removed and handled. After a period of curing in warm chambers they are autoclaved at pressures similar to those used in calcium silicate brick manufacture. In other types the initial heating in the moulds is omitted, stiffer mixes being used, while the dense boards are formed on machines which impart considerable pressure to compact the material.

Some properties of one type of the very lightweight calcium silicate insulation material and one type of calcium silicate bonded insulation board are given in Table VIII. These materials are resistant to heat and fire and are unaffected by steam, moulds or fungal growth, and organic

solvents. The dense board types are also fairly resistant to acids and are less brittle than the types of asbestos board bound with Portland cement.

No work is known to have been published on the constitution of the bond in these materials. It seems likely that it is essentially the same as in other autoclaved calcium silicate products, but there may be some reaction with the asbestos minerals affecting the phase formation.

V. Very High Strength Calcium Silicate Bonded Products

Although, as shown in Table I, the currently manufactured range of calcium silicate bricks extends only up to about 8000 lb/in² compressive strength when tested in the wet state, equivalent to about 10,000 lb/in² if tested dry, this does not by any means indicate a practical limit of strength. In the author's laboratory wet strengths of up to 12,000 lb/in² have been shown to be practicable with economic mixes and conditions of processing. The Russian material Silicalcit, which is produced widely in the form of building slabs, beams, pipes, tiles and paving slabs, is claimed [36, 37] to have strengths of up to 20,000 lb/in²; the material developed in W. Germany, known as Poreen, in which pipes of large diameter and paving slabs have been made, is said [38] to have strengths of the order of 12,000 lb/in². Details of all these processes are at present undisclosed, but they are all, it is understood, essentially the same as the calcium silicate bonded bricks, apart from the fact that the materials and mixes are specially chosen or treated to attain the high strengths.

Further confirmation of the high strengths obtainable with hydrated calcium silicate has been obtained by Taylor [39]. Dry compressive strengths of pressed materials made in the laboratory, with very fine silica and lime, of as much as 20,000 lb/in² at a density of 100 lb/ft³ and 36,000 lb/in² at a density of 130 lb/ft³ have been found. The mixes were made at the optimum lime/silica ratio, given as about $0.14 + 0.00009$ times the specific surface of the silica (cm²/g).

There appears to be considerable potential for development of use of autoclave-hardened calcium silicate bonded products based on lime as the raw material, into fields at present satisfied only by Portland cement products; in the U.S.S.R. such developments have already become important.†

VI. Calcium Silicate Fillers

Fillers are generally very fine inert powders included in compositions to modify the properties and to reduce consumption of more expensive active ingredients. The most important properties for this use are very

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fine particle size and high surface area; because of shape factors, these
properties are not necessarily closely related when considering different
sorts of filler. Although the fillers are inert, their surface energy and
packing characteristics are extremely important in their effects upon the
properties of the product.

Precipitated hydrous calcium silicates have been used as fillers, first
in the rubber industry and subsequently in the paint and plastics in-
dustry, since about 1930. Fineness and surface properties, rather than
chemical composition or constitution, have been given most attention
in the control of quality during manufacture.

Other materials used as fillers include fine clays, precipitated silica,

TABLE IX

Effect of calcium silicate filler loading upon the properties of a natural
rubber mix [41]. (Composition of mix: 100 parts natural rubber, 5 parts zinc
oxide, calcium silicate filler as shown, 2 parts accelerators, 3 parts sulphur,
3 parts stearic acid)

Loading of calcium silicate (parts by weight)	Curing [1] at 287° F (min)	Modulus at 300%	Tensile strength	Elongation at failure	Hardness	Tear strength (lb/in²)
21	20	430	4000	700	45	300
42	15	710	3930	660	51	520
63	20	1120	3090	550	62	450
84	10	1220	2860	550	63	470

[1] Period of optimum curing as judged by tensile strength.

hydrous aluminium silicate, whiting and precipitated calcium carbonate.
Each has its particular characteristics and advantages for specific uses.

In rubber manufacture any of these fillers is used with or in place of
carbon black, which is normally the principal ingredient other than the
rubber itself, conferring toughness and other useful properties. The
proportions of carbon black and/or any particular filler used depend upon
the properties required in the specific product being made. Thus, for one
product the abrasion resistance may be of dominant importance, for
another the tear strength, and for another the amount of elongation
under load and the tensile strength. All of these properties are modified
by the filler. Although, as mentioned above, the particle size is, for any
one type of filler, the major variable affecting its value in conferring
suitable properties to the product, for a given mean particle size, differ-
ences in shape or in chemical composition and structure may also be

important. For example, for shoe soles and heels it has been suggested [40] that certain resin-rubbers containing calcium silicate fillers wear better than those containing clay fillers.

As an example of the effect of the quantity of a calcium silicate filler upon the properties of a natural rubber mix, the data [41] reproduced in Table IX are of interest. The figures quoted should be regarded only as relative to each other, since they depend upon the qualities of the particular ingredients and upon the methods of test, but they serve to indicate the quantities of filler that may be usable.

A. MANUFACTURE

Since all calcium silicate fillers are made either by undisclosed proprietary processes or by patented processes, little can be said of them here. They are mostly, it is understood, based upon precipitation from sodium silicate solutions by calcium chloride, under closely controlled conditions of temperature, solution concentration and agitation. The sodium/silica ratio in the sodium silicate must be adjusted correctly. Washing of the precipitate after filtration, to remove sodium salts, must be very thorough and the drying method must be designed to avoid risk of overheating.

B. CHEMICAL COMPOSITION AND CONSTITUTION

The composition of some of the commercial silicate fillers is given in Table X. It is apparent from the lime/silica ratio that they are all essentially mixtures of hydrated silicates and hydrous silica; it is not known by the author whether this is because of expediency in manufacture or because their properties as fillers are better than those of a calcium silicate

TABLE X

Composition of some commercial hydrated calcium silicate fillers [44]

Trade name	CaO	SiO$_2$	CaO:SiO$_2$ molar ratio	Na$_2$O	Loss at 105°C	Loss on ignition	pH
Anchor calcium silicate	16	60	0·29:1	—	3	17·5	10
Calsil	10–11	69–70	0·16:1	2·3	—	15	10
Silene EF	18	64	0·30:1	—	5	15	10
Silmos A [1]	18·1	45·2	0·43:1	—	8	19	9·8
Tufknit	16·0	59·5	0·29:1	—	—	20	10·1

Header spanning: Analysis (per cent by weight)

[1] Also contains MgO, Al$_2$O$_3$ and Fe$_2$O$_3$.

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only. It is perhaps significant that they all have an equilibrium pH of about 10, corresponding to the equilibrium between C-S-H (I) and SiO_2.aq., whereas C-S-H (I) by itself would give pH values between about 10·5 and 12, depending upon the CaO/SiO_2 ratio [42]. These higher pH values may be unsuitable for some uses. The pH values shown in Table X are those quoted by the manufacturers and generally relate to suspensions of about 5% concentration.

The combined water/silica ratios, from the loss on ignition figures, range from 0·7 to 1·4. This is consistent with a mixture of C-S-H (I) or tobermorite and hydrous silica, dried at temperatures near to 100°C. Some of the fillers contain significant amounts of alkali (Na_2O) present—this is probably due to inadequate washing rather than to any intentional content. On the other hand, the presence of some MgO, Al_2O_3 and Fe_2O_3 in other of these products may be intended as modifying the properties.

Where the precipitation is made at fairly low temperatures in the presence of excess silica, the silicate phase will, it seems, be a C-S-H (I) of low lime/silica ratio (less than 1). If higher temperatures are used, with some time allowed for aging, there may be some crystallization of tobermorite, but it seems unlikely that this will be significant under conditions operating in industrial production. Treatment at higher temperatures in the autoclave will give tobermorite or even xonotlite [43], but no commercial fillers made in this way are known.

The user of fillers in the rubber and plastics industries is concerned mainly with the surface properties of the particles rather than with those of the material as a whole. Therefore, apart from the particle size and surface area, considered in a subsequent paragraph, there may be important differences in distribution of the calcium atoms which may affect the surface properties. Thus, it seems possible, even with particles in the millimicron size range, to have the calcium silicate (C-S-H (I)) present either as separate particles or as coatings on the surfaces of grains of hydrous silica. There has been a good deal of study of the behaviour of fillers in rubber [44, 45, 46] and some theoretical considera-tion of the nature of the surface and of the surface bond with hydrous silica.

C. PARTICLE SIZE, SURFACE AREA AND STATE OF AGGREGATION

One of the chief merits of the precipitated calcium silicates for use as fillers for rubber and plastics lies in the extreme fineness and repro-ducibility of particle size characteristics, which derive from the low solubility and from the control possible in the conditions of precipitation. A few figures quoted commercially are shown in Table XI, from which it may be seen that the particle size is generally in the range 20–50 mμ

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with corresponding surface areas of some 50–150 m²/g. This is comparable with values for most of the carbon black fillers used in the rubber manufacturing industry.

Since the commercial fillers are, as already indicated, made up of two components, C-S-H (I) and hydrous silica, the shapes of the particles must be expected to be of two types, the two-dimensional sheet crystallites of C-S-H (I) (see Chapter 21 and Volume 1, Chapter 5) and granular or irregular particles of hydrous silica. There may therefore be a wide range of particle dimensions above and below the mean particle diameters quoted.

TABLE XI

Physical properties of some commercial hydrated calcium silicate fillers [44]

Trade name	Surface area (m²/g)	Mean particle diameter (mμ)	Loose bulk density (lb/ft³)	Specific gravity	Refractive index
Anchor calcium silicate	—	50	—	—	—
Calsil	—	40	9·4	2·05	—
Fortafil A70	105	30	—	2·1	—
Microcal 160	—	30–50	9	2·1	1·47
Microcal 210	—	30–50	12	2·0	1·45
Silene EF	80	30	12	2·1	1·47
Silmos A	140–160	—	—	2·0	—
Tufknit CS	50	—	11	2·1	1·47

The state of aggregation of the particles of such powders, arising from flocculation during precipitation and any slight cementing together during drying, may also be a significant factor affecting use. Comparisons may be made of the relative aggregation of different fillers by use of the electron microscope or by oil-absorption or water-absorption tests [44, 47].

The quoted refractive indices and specific gravities of these commercial products shown in Table XI are all similar and are consistent with the constitution noted. The loose bulk densities, also shown in the table, do not vary widely; they are dependent upon particle size factors more than upon the specific gravity of the material.

VII. Lime-stabilized Soils

The immediate effect of an admixture of lime with soils of high clay content, in reducing the plasticity of the soil, has long been familiar to the farmer. This effect, and a further slow reaction between the lime

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and clay causing a progressive coherence and strength development in a compacted lime–clay mix, are now utilized by the civil engineer in road construction and other works [48]. This soil stabilization by lime, as it is called, is now being widely used with clay, clay-gravel and loess types of soil, for improvement of the sub-grades and construction of bases and sub-bases of roads. Use is most widespread in hot climates (e.g. Africa; Texas and Louisiana, U.S.A.) or where particularly suitable soils are found (Germany, with loess soils). Generally, about 5% by weight of lime is mixed with any layer of soil being stabilized, which may be 4–8 in thick. The mixing is generally done by machines which break up the soil and mix in the lime as they pass over the ground (mix-in-place methods) or, less commonly, by mixing in stationary mixing plant and transporting onto the site (pre-mix methods). The primary changes in plasticity of the clays are believed to be due to physico-chemical effects of base exchange in the clay minerals and of flocculation of the clay in the high pH environment given by the presence of lime. The longer term effect of cementation and strength development is due to a slow chemical reaction between the lime and clay minerals. Chemical tests show that the free lime gradually disappears during moist storage of such lime–clay mixes [49] and that new compounds must therefore be formed. If the minor components in clays (magnesia, iron oxide and alkalis) are ignored, this reaction falls within the $CaO-Al_2O_3-SiO_2-H_2O$ system and the end-products should be the same as for other reacting phases in that system, i.e. they should be hydrous calcium silicates, aluminates and alumino-silicates.

Although a great deal of work on soil stabilization by lime and on the mechanical and physical properties of the stabilized material has been published [50, 51], very little is known so far of the chemistry involved. Results of only a few investigations have been published [52, 53, 54] and they give no more than an indication of the reactions or products.

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ADDENDUM

The author, since writing this chapter, has had opportunity of studying in the U.S.S.R. the wider developments in the use of calcium silicate products mentioned briefly on p. 126. It is possible to add here only a short note on these developments which, with research carried out in relation thereto, would merit additional chapters in this book.

Autoclaved calcium silicate processes are now used in the U.S.S.R. on a very large scale for production of all types of building units for industrialized building techniques. Indeed the entire structures of some buildings, including floor and roof units, large external and internal wall units, staircases, beams, pillars and lintels, consist of these materials. According to the purpose being served, the units may be plain or reinforced, and consist of high or medium strength, dense ($D = 1\cdot8-2\cdot2$) or light weight aerated ($D = 0\cdot7-0\cdot8$) material. The minimum compressive strength for most types of unit in the dense materials is about 3000 lb/in² but some types are being produced with strengths of 10,000 lb/in² or more.

Two main types of process are used: the "Silicalcit" process which involves treatment of the whole of the sand and lime mixture in a high speed disintegrator which is said to produce highly reactive surfaces on